

PATENT SPECIFICATION



NO DRAWINGS

1,176,217

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International Classification:—C 08 b 21/26, 27/76

COMPLETE SPECIFICATION

Solid, Dry preparations of Water-Insoluble Dyestuffs and processes for their manufacture and use

We, CIBA LIMITED, a Body Corporate organised according to the laws of Switzerland, of Postfach, 4000 Basle 7, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- 5 In the application of certain water-insoluble colorants, namely, pigments, vat dyestuffs and so-called disperse dyestuffs, it is of great importance that the colorants be in a state of fine and uniform division. These kinds of colorants are therefore often used in the form of specially manufactured preparations which contain special additives in addition to the finely divided colorant. The additives selected must be capable of dissolving in the application medium used, which may be water, a liquid organic medium or a melt, and they must not adversely affect the application process or the properties of the coloured product. Depending on the method by which the preparations are to be applied, the additives may be, for example, synthetic or natural polymers free from any pronounced surface-active properties, for example, cellulose acetate, ethyl cellulose, polyvinyl chloride and the copolymers thereof, polyacrylonitrile, polyamides, polyolefines and refined colophony, or they may be ionic or nonionic surface-active compounds, for example, the condensation product of β -naphthalene sulphonic acid and formaldehyde, partially desulphonated lignin sulphonate or the condensation product of 1 mol of octylphenol and 8 to 10 mols of ethylene oxide.
- 10 The present invention is based on the surprising observation that by the use of hydroxyalkylcellulose ethers as additives, solid dry dyestuff preparations of water-insoluble colorants may be obtained which disperse readily, that is to say, generally without the need for special processing steps or great mechanical force, in aqueous application media, certain liquid organic application media and in the melts of certain organic substances, in a manner such that the insoluble colorant is liberated in its original state of fine and uniform division and is uniformly dispersed in the application medium. It has also been observed that neither the application process nor the properties of the coloured products are adversely affected by the use of hydroxyalkyl-cellulose ethers as additives to pigments, vat dyestuffs or disperse dyestuffs, this applying to an unexpectedly large number of widely differing applications. By hydroxyalkyl-cellulose is meant, in addition to the actual hydroxyalkylcellulose ethers, for example, hydroxyethyl cellulose, hydroxypropyl cellulose or hydroxyethylhydroxypropyl cellulose, also the alkylhydroxyalkylcellulose ethers, that is to say, those cellulose ethers in which

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not all etherically-bound alkyl radicals contain hydroxyl groups, for example, ethylhydroxyethyl cellulose, methylhydroxyethyl cellulose or methylhydroxypropyl cellulose. The hydroxyalkyl cellulose ethers may be free from ionic groups. Furthermore, by hydroxyalkyl groups are also meant hydroxyalkyl-monoxyalkylene and hydroxyalkyl-polyoxyalkylene groups.

Depending on the degree to which they are substituted and on the nature of the substitution, the various hydroxyalkylcelluloses display different solubility behaviour in aqueous media, liquid organic media and melts of organic substances, and also different thermoplastic properties. Accordingly, those hydroxyalkylcelluloses are chosen as additives for the colorant preparations which are soluble in the application medium to be used or are compatible with it and which do not adversely affect the application process. Thus, hydroxyethyl cellulose is the substance which is specially suitable as the additive in colorant preparations which are to be used in aqueous application media at an elevated temperature, because unlike, for example, hydroxypropyl cellulose, it remains soluble in water even when the temperature is raised. When, on the other hand, the preparations are to be applied in certain liquid organic media, for example, an alcohol or dimethylformamide, or in the melts of thermoplastic synthetic materials, the principal additives used are, for example, hydroxypropyl cellulose, hydroxyethylhydroxypropyl cellulose and the water-insoluble properties of ethylhydroxyethyl cellulose. When the preparations are to be applied in the melts of thermoplastic synthetic materials, it is specially advantageous if the cellulose ethers indicated are themselves thermoplastic. The quantitative ratio of colorant to cellulose ether in the colorant preparation is at most 9:1; however, it is preferably between 9:1 and 1:4, and especially between 4:1 and 1:4. The colorant preparations may be used in the form of powders or aqueous pastes; the latter form may be desirable when application is to be effected in an aqueous medium. It has an advantage over many colorant preparations in that it is frost-resistant, that is to say, the quality of the aqueous preparation is not impaired by freezing and thawing.

Manufacture of the colorant preparations from the water-insoluble colorants and the above-mentioned cellulose ethers, for example, a hydroxyalkyl cellulose free from ionic groups which is soluble in water and/or organic liquids, may be effected by various known methods, the use of water-soluble hydroxyalkylcelluloses having the advantage that manufacture of the preparations may be carried out in aqueous systems. For example, manufacture may be effected simply by mixing the components in the dry state or especially in a liquid medium, by grinding the components together in the dry state or especially in a liquid medium, for example, in a ball mill, an attrition mill or a sand mill, or by kneading the components in a kneading apparatus, for example, in a Werner & Pfleiderer sigma-type kneader, in which process a liquid which dissolves the hydroxyalkyl-cellulose under the kneading conditions is used or, if a water-insoluble hydroxyalkyl-cellulose is employed, use may be made of a comminuting assistant, for example, finely powdered sodium chloride. Alternatively, it is possible to grind the dyestuff alone in a liquid medium until it has the desired degree of fineness and to add subsequently a hydroxyalkyl-cellulose soluble in the liquid medium used. The products in liquid or paste form obtained by the aforementioned processes is converted into a dry form by evaporation, spray-drying, freeze-drying, and so forth. Another method of producing dry colorant preparations is as follows: a suspension of the water-insoluble colorant in which the cellulose ether is dissolved which has been prepared by grinding in a liquid medium is treated with another liquid which is at least partially miscible with the liquid grinding medium, but which does not dissolve the cellulose ether used. This precipitates the cellulose ether on to the suspended colorant and the product may then be isolated by filtration and dried.

Depending on the purpose for which the colorant preparations of the invention are to be used, they may contain, in addition to the water-insoluble colorants and the hydroxyalkyl-cellulose ethers, further additives, for example, plasticizers, fungicides and especially surface-active substances (tensides). These additives may be incorporated in the preparations at any stage in the manufacturing process which is convenient, that is to say, prior to, simultaneously with or subsequent to addition of the hydroxyalkylcellulose to the colorant.

A very wide variety of compounds may be used as water-insoluble colorants, depending on the field of application; this can be seen from the many possibilities for application indicated below for colorant preparations containing a hydroxyalkylcellulose ether as additive. Pigments that may be mentioned are, for example, natural and synthetic inorganic pigments and, in particular, synthetic organic pigments, for example, those belonging to the nitro, azo, phthalocyanine, thioindigo,

- anthraquinone, perinone, perylene, dioxazine or quinacridone classes. Vat dyestuffs that are suitable are principally those derived from anthraquinone and other polycyclic or heterocyclic quinones, vat dyestuffs of the indigo series and the perylenetetracarboxylic acid diimide series, and also derivatives of naphthalenetetracarboxylic acid. Suitable disperse dyestuffs are, for example, those belonging to the nitroarylamine, styryl and especially the azo and anthraquinone series. Many members of these classes of dyestuffs and pigments are included in the Colour Index, 2nd Edition, 1956, Vol. 1, pages 1655—1742, and Vol. 2, pages 2419—2564 and 2697—2814.
- When the colorant preparations of the invention contain pigments as water-insoluble colorants they may be used in an anhydrous form, for example, for pigmenting *thermoplastic synthetic materials* and films. In preparations containing pigments it is advantageous that the major proportion by weight of the pigment should have a particle size of $1\ \mu$ and below. The hydroxyalkylcelluloses which are specially suitable for use as additives in pigment preparations are those which are themselves thermoplastic and capable of being extruded, for example, hydroxypropyl cellulose and hydroxyethylhydroxypropyl cellulose. The surprising observation has been made that these preparations can be used for a very wide variety of synthetic materials, for example, plasticized polyvinyl chloride, rigid polyvinyl chloride and copolymers of vinyl chloride, polyvinylidene chloride, polyolefines, for example, polyethylene, polypropylene or polyisobutylene, polystyrene and copolymers of acrylonitrile, butadiene and styrene, polymethacrylates, polyamides, polyurethanes or cellulose derivatives, for example, cellulose acetate, ethyl cellulose or celluloid.
- The new pigment preparations may also be used for *pigmenting paints* and lacquers, especially for pigmenting paints and lacquers that can be diluted with water. The paints may be of the kind which are based on water-soluble binders and especially water-soluble synthetic resins which, subsequent to application, are rendered water-insoluble by a heat treatment; it may be specially advantageous in this particular use if the hydroxyalkylcelluloses to be used in accordance with the invention as additives are capable of being rendered insoluble by cross-linkage (*via* their hydroxy groups) with polyfunctional compounds. Furthermore, the pigment preparations of the invention may be used for pigmenting emulsion paints based on aqueous latices of polymers or for pigmenting water colours. They may also be used for pigmenting lacquering baths in the electrophoretic application of lacquer coatings to surfaces (electrodeposition).
- The pigment preparations of the invention may also be used for pigmenting paints and lacquers based on organic solvents and water-insoluble binders, in so far as the hydroxyalkylcellulose used is soluble in the lacquer solvent or mixture of solvents and is compatible with the binder or binders.
- Another field of application for the new pigment preparations is the coloration of *printing inks*. For example, they can be used for pigmenting printing inks which can be diluted with water and which are based on water-soluble binders, for example, inks for printing wallpapers. They may also be used for pigmenting water-based, water/alcohol-based or alcohol-based inks for intaglio printing, flexographic printing or screen printing, as used, for example, for printing on paper. The alcohol-solubility, for example, of hydroxypropylcellulose, is specially advantageous in the case of alcohol-soluble printing inks. Furthermore, it is possible for the hydroxyalkylcelluloses to cross-link with reactive binders, which for example, increases wet strength. By virtue of the fact that the additives are capable of cross-linkage with polyfunctional compounds, the preparations of the invention are specially suitable for the coloration and printing of decorative papers which are subsequently to be processed into laminates together with reactive resins.
- The pigment preparations of the invention may also be used for the *spin-coloration of man-made fibres*, it being possible to apply them in melts, aqueous solutions and organic solutions. For example, anhydrous forms of the new pigment preparations are suitable for pigmenting polyolefine and polyamide fibres in the melt-spining process. The new pigment preparations in dry form or in the form of aqueous pastes may be used for the spin-coloration of fibres made from aqueous solutions, for example, regenerated cellulose fibres of all kinds. It is specially advantageous that, as is known, the properties of the viscose fibres are not impaired by the hydroxyalkylcelluloses used as additives, and that, in particular, hydroxyethylcellulose is only slightly surface-active, which is specially desirable in the spin-coloration of viscose fibres of high wet strength. Finally, the new solid, dry pigment preparations may also be used for the spin-coloration of synthetic fibres which are spun from the kind of organic solvent or

mixture of solvents in which the hydroxyalkylcelluloses, used as additives display adequate solubility. For example, pigment preparations based on hydroxypropylcellulose may be used for the spin-coloration of polyurethane fibres made from a solution in dimethylformamide, or polyvinyl chloride fibres made from, for example, a solution in tetrahydrofuran or cyclohexanone, or cellulose triacetate fibres made from, for example, a solution in a mixture of methylene chloride and alcohol or a solution in dimethylsulphoxide. The new pigment preparations may naturally also be used for the mass-coloration of films, for example, cellophane, in a manner analogous to that used for the spin-coloration of synthetic fibres.

Another field in which the pigment preparations of the invention may be used, either in a dry form or in the form of an aqueous paste, is the dyeing of *paper*, especially the pulp-dyeing of paper. It is specially advantageous in this field of application that, as is known, the cellulose ethers used also act as retention agents. Because of the ability of the hydroxyalkylcelluloses used in the preparations of the invention to cross-link with polyfunctional compounds, paper pulp-dyed in this manner is also specially suitable for use as decorative paper which is to be processed into laminates together with reactive resins.

The pigment preparations of the invention are also suitable for pigmenting *leather finishes*, in which application it is specially advantageous that the hydroxyalkylcelluloses used as additives can be rendered water-insoluble by cross-linkage (via the hydroxyl groups) with polyfunctional compounds, for example casein.

The pigment preparations of the invention are also suitable for pigmenting printing pastes and dyeliquors used in the *pigment printing or pigment dyeing of woven knitted or non-woven textile fabrics*. In this application, too, it is specially advantageous that the hydroxyalkylcelluloses can be rendered insoluble by cross-linkage with resin precursors that are present when the latter are polymerized to form resins, for example, melamine-urea resins, melamine-formaldehyde resins, urea-formaldehyde resins or acrylic resins.

The pigment preparations of the invention may also be used for pigmenting *many other materials*, for example, cement wall and ceiling plaster, soaps, waxes, coloured pencils, inks and water-colour paints and cosmetic preparations.

When the colorant preparations of the invention contain *vat dyestuffs* or *disperse dyestuffs* as water-insoluble colorants instead of pigments, they may be used either in dry form or in the form of aqueous pastes for dyeing or printing *textile materials*. When used for these purposes they are applied by the known methods for printing or dyeing with vat dyestuffs or disperse dyestuffs.

The following Examples illustrate the invention. Unless otherwise stated, the parts and percentages are by weight.

EXAMPLES

I. *Manufacture of preparations*

The preparations may be manufactured by the different processes described below under 1); naturally other processes of manufacture may be employed in addition to those indicated. The dyestuffs used in the various processes are more closely defined in Section 2) and the hydroxyalkylcellulose ethers used are more closely described in Section 3). Tensides are also added in some cases, and these are more closely defined in Section 4). The Table in Section 5) lists the preparations made by the methods indicated under 1) using the products listed under 2) and 3) and, in some cases, 4).

1) *Processes*

1a 10 Parts of colourant and 90 parts of water are ground in a sand mill until the desired degree of fineness has been achieved. After grinding, 100 parts of an aqueous solution containing 15 parts of hydroxyalkylcellulose ether (HAC) are added, the batch is well homogenized and the resulting dispersion is spray-dried (exhaust air 80°C). A loose powder is obtained consisting of 40% colourant and 60% HAC.

1b The process is analogous to 1a, but the HAC solution is added in an amount such that the products consist of 50% colourant and 50% HAC.

1c The process is analogous to 1a, but the HAC solution is added in an amount such that the products consist of 60% colourant and 40% HAC.

2 10 Parts of colourant, 1 part of HAC and 89 parts of water are ground in a sand mill until the desired degree of fineness has been achieved. After grinding, a further 9 parts of HAC are dissolved in the batch so that the colourant/HAC ratio is 1:1. The dispersion so obtained is spray-dried (exhaust air 80°C).

- 3a 5 Parts of colourant, 5 parts of HAC and 90 parts of water are ground in a sand mill or bead mill until the desired degree of fineness has been achieved (for example, 6 to 12 hours). The ground material is then separated from the grinding elements and spray-dried. A loose powder is obtained consisting of 50% colourant and 50% of HAC. 5
- 3b The process is analogous to 3a, except that the colourant/HAC ratio is 3:2, which means that a product containing 60% of colourant and 40% of HAC is obtained.
- 3c The process is analogous to 3a, except that the colourant/HAC ratio is 7:3, which means that a product containing 70% of colourant and 30% of HAC is obtained.
- 10 3d The process is analogous to 3a, except that the colourant/HAC ratio is 4:1, which means that a product containing 80% of colourant and 20% of HAC is obtained. 10
- 4 Grinding is carried out in a manner analogous to that described under 3a. However, working up of the ground material is effected in the following manner: 1 part of the aqueous batch, in which the hydroxyalkylcellulose is dissolved and the colourant dispersed, is treated with 3 parts of acetone while stirring. This precipitates the hydroxyalkylcellulose out of solution and the colourant is coprecipitated. The flocculent suspension so formed is filtered, the filter cake is washed well with acetone and subsequently dried in a vacuum cabinet at 40°C. The dried material is then pressed through a sieve having a mesh size of 0.5 mm. 15
- 20 5 Grinding is carried out in a manner analogous to that described under 3a. However, working up is effected by freeze-drying and not by spray-drying or precipitation. 20
- 6 8 Parts of colourant, 4 parts of HAC, 4 parts of the anionic tenside (TA) defined under 4) and 84 parts of water are ground in a sand or bead mill until the desired degree of fineness has been achieved. The batch is then separated from the grinding elements and spray-dried. A loose powder is obtained. 25
- 7 The process is analogous to 6, except that 9 parts of colourant, 6 parts of HAC, 3 parts of the non-ionic tenside (TB) defined under 4) and 82 parts of water are used.
- 30 8a 10 Parts of colourant and 10 parts of HAC are ground for 6 to 12 hours in a sand mill or bead mill in 80 parts of benzine (which is *not* a solvent for the HAC used). During grinding, colourant and HAC combine physically to form a phase which has the appearance of being homogeneous. This is separated from the liquid by filtration and dried in a vacuum cabinet at 60°C. 30
- 35 8b The process is analogous to 8a, except that water is used as the grinding medium instead of benzine. 35
- 9a 5 Parts of colourant are ground in a solution of 5 parts of HAC in 90 parts of ethanol in a sand mill or bead mill until the desired degree of fineness has been achieved. The colourant preparation is precipitated out of the batch by the addition of ether and worked up by filtration, washing and drying in a vacuum cabinet. 40
- 9b The process is analogous to 9a, except that methylethylketone is used as grinding medium instead of ethanol, and water is used as precipitant instead of ether.
10. 60 Parts of colourant, 60 parts of HAC and 125 parts of water are kneaded in a laboratory kneader until a homogeneous paste in which the colourant has the desired degree of fineness is obtained. This may be used as it is or it may be worked up by drying in a vacuum cabinet or by spray-drying subsequent to dilution with water, depending on the purpose for which it is to be used. 45
- 11 85 Parts of colourant, 85 parts of HAC and 37 parts of glycolmonoethyl ether are kneaded and worked up in a manner analogous to that described under 10.

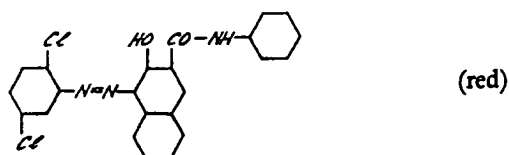
12 1 Part of colourant, 1 part of HAC, 4 parts of sodium chloride and 0.6 part of methylethylketone are kneaded in a laboratory kneader until the pigment has acquired the desired degree of fineness. 6 Parts of water are then added to the dough, which breaks down to a granulate. The granulae is then ground wet in a toothed colloid mill in an optional amount of water. The suspension so obtained is filtered, the filter cake is washed with water until free from chloride and then dried in a vacuum cabinet at 65°C. 5

13 1 Part of colourant and 1 part of HAC are ground in a porcelain ball mill and the resulting preparation, which has the appearance of being homogeneous is used as it is. 10

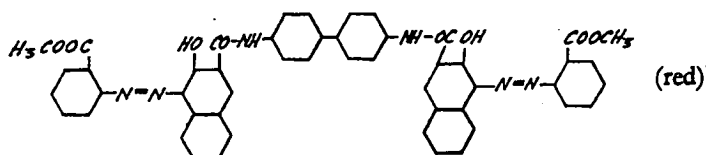
14 25 Parts of colourant are dispersed in a solution of 25 parts of HAC in 475 parts of water with the aid of a toothed disc mill (dissolver), and the suspension so obtained is spray-dried.

2) Colourants

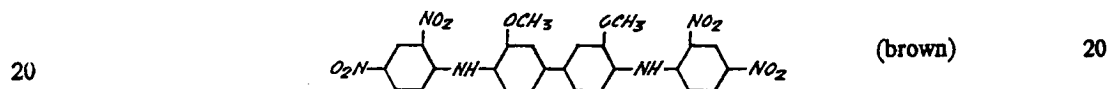
15 A. Monoazo dyestuff of the formula 15



B. Disazo dyestuff of the formula



C. Nitro dyestuff of the formula



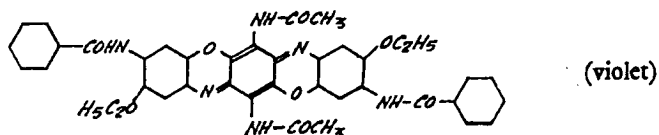
D. β -Copper-phthalocyanine

(blue)

E. Indigo

(blue)

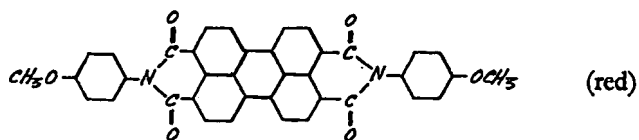
F. Dioxazine dyestuff of the formula



G. γ -Quinacridone

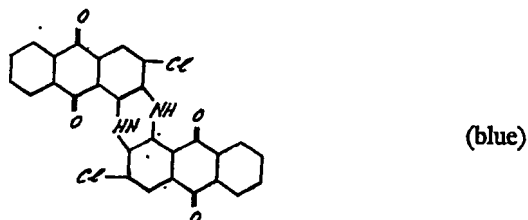
(red)

H. Perylene dyestuff of the formula

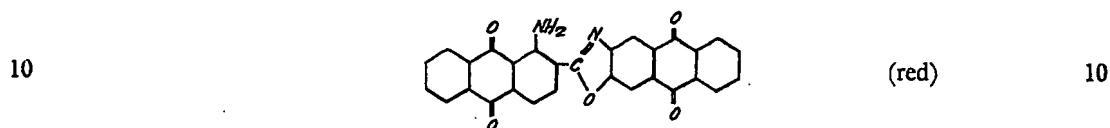


- 5 I. Carbon black (Philblack O; Phillips Petroleum Company)
 K. Iron oxide red (1027; Kalichemie, Hannover) 5
 L. Titanium dioxide (Rutile Kronos RN56; Titangesellschaft G.m.b.H.)

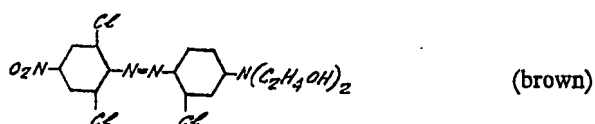
M. Vat dyestuff of the formula



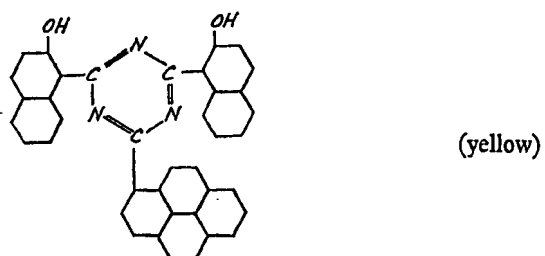
N. Vat dyestuff of the formula



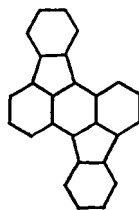
O. Disperse dyestuff of the formula



P. Pigment of the formula

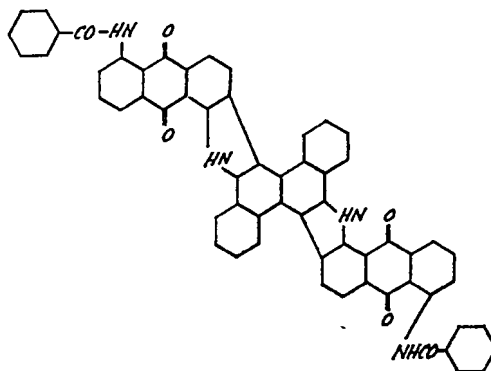


Q. Pigment of the formula



(orange)

R. Vat dyestuff of the formula



(brown)

5 3) *Hydroxyalkylcellulose* 5
 Natrosol 180 L = hydroxyethylcellulose ether; mean degree of substitution = 1.8;
 viscosity of a 5% solution in water at 25°C = 75—150 cps. Manufacturer: HER-
 CULES

10 Natrosol 250 L = hydroxyethylcellulose ether; mean degree of substitution = 2.5;
 viscosity of a 5% solution in water at 25°C = 75—150 cps. Manufacturer: HER-
 CULES 10

Modocoll E 20 = ethylhydroxyethylcellulose ether; viscosity of a 2% solution in
 water at 20°C = 50—100 cps. Manufacturer: Mo och Domsjö, Sweden.

15 *Modocoll E 100* = ethylhydroxyethylcellulose ether; viscosity of a 2% solution in
 water at 20°C = 250—400 cps. Manufacturer: Mo och Domsjö, Sweden. 15

EHEC extra low = water-insoluble ethylhydroxyethylcellulose ether; viscosity of
 a 5% solution in an 8:2 mixture of toluene and ethanol at 25°C = 10—19 cps. Manu-
 facturer: HERCULES

20 *EHEC low* = water-insoluble ethylhydroxyethylcellulose ether; viscosity of a 5%
 solution in an 8:2 mixture of toluene and ethanol at 25°C = 20—35 cps. Manufac-
 turer: HERCULES 20

EHEC high = water-insoluble ethylhydroxyethylcellulose ether; viscosity of a 5%
 solution in an 8:2 mixture of toluene and ethanol at 25°C = 125—250 cps. Manufac-
 turer: HERCULES

25 *Klucel E* = hydroxypropylcellulose ether; viscosity of a 10% solution in water at
 25°C = <300 cps. Manufacturer: HERCULES 25

Klucel L = hydroxypropylcellulose ether; viscosity of a 5% solution in water at
 25°C = 75—150 cps. Manufacturer: HERCULES

30 *Klucel 7* = hydroxypropylcellulose ether; viscosity of a 5% solution in water at
 25°C = 150—400 cps. Manufacturer: HERCULES 30

4) *Tensides*

TA = anionic tenside: condensation product of β -naphthalene sulphonic acid and formaldehyde, sodium salt.

TB = non-ionic tenside; condensation product of 1 mol of octylphenol and 8 to 10 mols of ethylene oxide.

5) Table of preparations

Prep. No.	Made by process	Colourant	Hydroxyalkyl-cellulose ether	Tenside	Colourant content in per cent
A 1	6	A	Natrosol 250 L	TA	50
A 2	3a	A	Klucel L	—	50
B 1	3a	B	Natrosol 250 L	—	50
B 2	4	B	„	—	50
B 3	6	B	„	TA	50
B 4	6	B	Natrosol 180 L	TA	50
B 5	9a	B	Klucel E	—	50
B 6	3a	B	Klucel L	—	50
B 7	8a	B	„	—	50
B 8	7	B	„	TB	50
B 9	3a	B	Klucel J	—	50
B 10	9b	B	EHEC extra low	—	50
B 11	8b	B	EHEC high	—	50
C 1	1c	C	Natrosol 250 L	—	60
C 2	2	C	„	—	50
C 3	3a	C	„	—	50
C 4	5	C	„	—	50
C 5	3d	C	„	—	80
C 6	6	C	„	TA	50
C 7	3b	C	Natrosol 180 L	—	60
C 8	3d	C	„	—	80
C 9	1a	C	Klucel L	—	40
C 10	1b	C	„	—	50

Prep. No.	Made by process	Colourant	Hydroxyalkyl-cellulose ether	Tenside	Colourant content in per cent
C 11	3a	C	Klucel L	—	50
C 12	3c	C	„	—	70
C 13	5	C	„	—	50
C 14	3a	C	Modocoll E 20	—	50
D 1	3a	D	Natrosol 250 L	—	50
D 2	3a	D	„	—	50
D 3	10	D	Natrosol 250 L	—	50
D 4	6	D	„	TA	50
D 5	3a	D	Natrosol 180 L	—	50
D 6	3a	D	Klucel E	—	50
D 7	3a	D	Klucel L	—	50
D 8	11	D	„	—	50
D 9	6	D	„	TA	50
D 10	7	D	„	TB	50
D 11	3a	D	Klucel J	—	50
D 12	9b	D	EHEC extra low	—	50
D 13	12	D	EHEC low	—	50
E 1	6	E	Natrosol 250 L	TA	50
E 2	3a	E	Modocoll E 100	—	50
F 1	4	F	Natrosol 250 L	—	50
F 2	3a	F	Klucel L	—	50
G 1	4	G	Natrosol 250 L	—	50

Prep. No.	Made by process	Colourant	Hydroxyalkyl-cellulose ether	Tenside	Colourant content in per cent
G 2	6	G	Natrosol 250 L	TA	50
G 3	3a	G	Klucel L	—	50
H 1	4	H	Natrosol 250 L	—	50
H 2	6	H	„	TA	50
H 3	3a	H	Klucel L	—	50
I 1	3d	I	Natrosol 250 L	—	80
I 2	4	I	„	—	50
I 3	6	I	„	TA	50
I 4	3a	I	Klucel L	—	50
K 1	4	K	Natrosol 250 L	—	50
K 2	3a	K	Klucel L	—	50
L 1	13	L	Klucel E	—	50
L 2	14	L	Klucel L	—	50
M 1	4	M	Natrosol 250 L	—	50
M 2	6	M	Natrosol 250 L	TA	50
M 3	3a	M	Klucel L	—	50
N 1	4	N	Natrosol 250 L	—	50
N 2	6	N	„	TA	50
N 3	3a	N	Klucel L	—	50
O 1	3a	O	Natrosol 250 L	—	50
O 2	3a	O	Klucel L	—	50

Note:

— Preparation I 1 is in paste form.

— The percentage of colourant is based on the total solids content.

II. Application of the preparations

The examples of application given in the following provide a survey of the possible uses of the colourant preparations described under I, without, however, imposing any limitations. Unless otherwise stated, the preparations are used in the form of a dry powder. However, they may also be used in the form of pastes, depending on the nature of the application.

1. Pigmenting thermoplastic synthetic materials

1.1. Plasticized PVC

A mixture is prepared from
 0.08 part of Preparation B5
 1.0 part of titanium dioxide Rutile Kronos RN 56
 13.3 parts of polyvinyl chloride Type G (Lonza) and
 7.3 parts of DOP = di-(2-ethylhexyl)-phthalate

and worked to and fro on a two-roller mill for 5 minutes at 150°C. An evenly coloured film is obtained. There is no indication that the hydroxyalkylcellulose has an influence on the fastness to migration. Equally good results may be achieved by replacing Preparation B5 with any one of the following preparations: B6, B7, B8, B9, B10, B11, C9, C11, C12, C13, D6, D7, D8, D10, D11, D12, D13, F2, G3, H3, I4, L1, L2 and N.3

1.2 Polyethylene

99.9 parts of Hostalen GF 5250 (Hoechst) and
 0.1 part of Preparation B9
 are injection moulded twice at 220°C in a screw-type injection moulding machine. The moulded pieces are very evenly coloured and display good distribution of pigment. Equally good results may be achieved by replacing Preparation B9 with Preparation D7 or D8.

1.3 Polypropylene

a) Injection moulding

99.9 parts of Moplen AS 50 (Montecatini) and
 0.1 part of Preparation D7
 are injection moulded twice at 230°C in a screw-type injection moulding machine. The moulded pieces are very evenly coloured and display good distribution of pigment. Equally good results may be achieved by replacing Preparation D7 with Preparation D8.

b) Blown film

A blown film having a thickness of about 60 μ is made by the customary process from
 99.2 parts of Propathene GPE 33 (ICI) and
 0.8 part of Preparation D6.
 The film is very evenly coloured and displays good pigment dispersion. Equally good results may be achieved by replacing Preparation D6 with Preparation D7.

1.4 Polystyrene

99.9 parts of Polystyrol III C (BASF) and
 0.1 part of Preparation B9
 are injection moulded twice at 220°C in a screw-type injection moulding machine. The moulded pieces are very evenly coloured, display very good pigment dispersion and good transparency. A single injection moulding operation using Preparations C10, C12, D7 or D8 instead of Preparation B9 produces coloured moulded pieces displaying excellent transparency.

1.5 ABS

99.9 parts of Cyclolac T (Marbon Chemical) and
 0.1 part of Preparation B9
 are injection moulded once at 220°C in a screw-type injection moulding machine. The moulded pieces are very evenly coloured and display good pigment dispersion. Equally good results may be achieved by replacing Preparation B9 with Preparation C10, C12, D7 or D8.

1.6 Polymethacrylate

99.9 parts of Plexigum N6 (Roehm & Haas, Germany) and
 0.1 part of Preparation B9

- are injection moulded twice at 220°C in a screw-type injection moulding machine. The moulded pieces are very evenly coloured, display good pigment dispersion and very good transparency. Good results may also be achieved by replacing Preparation B9 with Preparation B10, D7, D8, D12 or D13. A single injection moulding operation is sufficient when using Preparations C10 and C12. Moulded pieces coloured with Preparations C10, C12, D7 and D8 display excellent transparency. 5 5
- 1.7 Polyamides**
- a) **PA 6**
- 99.9 parts of Ultramid BMK (BASF) and 0.1 part of Preparation B9 10 10
- are injection moulded twice at 260°C in a screw-type injection moulding machine. The moulded pieces are evenly coloured and display very good pigment dispersion. Very good results may also be achieved by replacing Preparation B9 with Preparations B10, C10, C12, D7, D8, D12 and D13.
- b) **PA 12** 15 15
- 99.9 parts of Vestamid X (Chemische-Werke Huels) and 0.1 part of Preparation B9
- are injection moulded twice at 220°C in a screw-type injection moulding machine. It is possible to replace Preparation B9 with Preparation B10, C10, C12, D7 or D8. All moulded pieces are very evenly coloured and display very good pigment dispersion. 20 20
- 1.8 Cellulose derivatives** (Cellulose acetate)
- 99.93 parts of Cellidor AM (Bayer) and 0.07 part of Preparation B9
- are injection moulded twice at 200°C in a screw-type injection moulding machine. The moulded pieces are evenly coloured and display very good pigment dispersion. A single moulding cycle is sufficient to produce moulded pieces having very good transparency when Preparation B9 is replaced by Preparation C10, C12, D7 or D8. 25 25
- 2. Foam plastics**
- 2.1. Polyurethane foam**
- 0.14 part of Preparation B9 is stirred into 20 30
- 20 parts of Desmophen 1800 (Bayer) and finely dispersed therein
- 7.5 parts of Desmodur T 56 (Bayer) are added and the whole is well mixed.
- 2 parts of a catalyst consisting of
- 6 parts of Desmorabit (Bayer)
- 3 parts of Disperser OH 35 35
- 3 parts of Additive SM and
- 2 parts of water
- are added and the batch is homogenized by a short stirring by means of a high-speed stirring device. The reaction mixture is allowed to stand for 1 hour to foam and cure. The foam obtained is very evenly coloured and pigment dispersion is satisfactory. 40 40
- Equally good results are obtained by replacing Preparation B9 with Preparation C10, C12, D7 or D8.
- 3. Paints and lacquers**
- 3.1 Water-soluble alkyd-melamine stoving lacquer**
- Brown Preparation C12 (70% pigment) is stirred into a water-soluble alkyd-melamine stoving lacquer (CIBAMIN WM 31, CIBA) with TiO₂ pigment in a ratio of 10:90. The lacquer is applied by means of a film drawing device and also with a spray gun, and subsequently stoved for 30 minutes at 150°C. In both cases very even coatings are obtained which display good pigment dispersion. 45 45
- The preparation may also be used in the form of an aqueous paste in the above application instead of in a dry form. 50 50
- 3.2 Aqueous emulsion paint**
- 2 parts of Preparation C12 are stirred into
- 98 parts of Eclasis A (PVA emulsion paint TiO₂ white paste, Messrs. Eklatin, Solothurn). 55 55
- Very even colouration is achieved with good dispersion of the preparation. The paint may be applied with a film drawing device or by means of a sheepskin roller.

The preparation may also be used in the form of an aqueous paste in the above application instead of in a dry form.

The following preparations are also suitable for pigmenting emulsion paints in the same manner: A1, A2, B1, B2, B3, B4, B5, B6, B8, C1, C2, C4, C6, C7, C8, C10, C11, C13, D1, D3, D4, D5, D6, B8, D9, E1, E2, F1, F2, G1, G2, G3, H1, H2, H3, I1, I2, I3, M2, M3, N2 and N3.

When, for example, Preparation C11 is frozen at a temperature of -14°C and then thawed prior to spray-drying, the paste shows the same dispersion stability and fine division of pigment as a paste which has not been frozen and thawed and gives the same quality of coating when applied in an aqueous PVA emulsion paint.

3.3 *Electro-coating*

Preparations D1 and D6 in the form of aqueous pastes are used for pigmenting an aqueous alkyd-melamine lacquer (CIBAMIN WM 31) which is applied electrophoretically to a) tin plate and b) phosphated iron. Application: 60 v; 2.5 amp; 30 seconds and 80 v; 4 amp; 30 seconds. The coatings are cured for 30 minutes at 150°C . The electrophoretically applied coatings display a much better gloss than coatings applied by means of a spray gun or a film drawing device. It has been found that the hydroxyalkylcellulose has an advantageous effect on the stability of the dispersion.

3.4 *Nitrolacquers.*

3.4.1. *Alcohol-soluble nitrolacquer*

2.8 Parts of Preparation B9 are stirred into 500 parts of a nitrolacquer having the following composition

520 parts of nitrocellulose NP 15
280 parts of *n*-butanol
104 parts of dibutylphthalate
660 parts of ethanol
332 parts of glycolmonoethylether and
332 parts of methylethylketone

for about 1 hour by means of a two-bladed stirrer. The lacquer so obtained, in which the colourant is extremely finely dispersed, produces coatings of great brilliance, tinctorial strength and outstanding transparency. Equally good results may be achieved by replacing Preparation B9 with Preparation B5, B6, B7, B8, B10, D6, D7, D8, D11, D12, F2, G3, H3, L1 or L2.

Preparations made by processes 9a or 9b may also be used in the form of the solvent paste.

3.4.2. *Ester-soluble nitrolacquer*

2.8 Parts of Preparation D12 are stirred into 500 parts of a nitrolacquer having the following composition

85 parts of nitrocellulose E 220 containing 18% of DOP
75 parts of ethylacetate
75 parts of butylacetate and
65 parts of methylethylketone

for about 1 hour by means of a two-bladed stirrer. The lacquer so obtained, in which the colourant is very finely dispersed, produces coatings of great brilliance, tinctorial strength and outstanding transparency. Equally good results may be obtained by replacing Preparation D12 with Preparation D 13.

3.5. *Composite nitrocellulose lacquer*

2.5 Parts of Preparation B10 are stirred into 500 parts of a composite nitrocellulose lacquer having the following composition:

1464 parts of nitrocellulose E 220 containing 18% DOP
600 parts of ethylacetate
3000 parts of butylacetate
948 parts of *n*-butanol
300 parts of diacetone-alcohol
540 parts of glycolmonoethylether
612 parts of Cibamine M 96 (75% strength in *n*-butanol) [CIBA]
1250 parts of Duraplex ND—78 (60% strength in Xylene) (Rohm & Hass)
336 parts of dioctyl phthalate (DOP)
1740 parts of toluene and
1224 parts of xylene

for about 1 hour by means of a two-bladed stirrer. The lacquer so obtained in which the colourant is very well dispersed, produces coatings of great brilliance, tinctorial strength and outstanding transparency. Equally good results may be obtained by using Preparation D12 instead of Preparation B10.

5 Preparations made by processes 9a or 9b may also be used in the form of the solvent paste. 5

4. *Printing inks*

4.1. *Organic printing inks*

10 5 parts of Preparation D7
8 parts of nitrocellulose A 250 (18% dibutylphthalate)
10 parts of glycolmonoethylether
20 parts of methylethylketone and
57 parts of ethanol

15 are homogenized for 15 minutes by means of a toothed disc stirrer. The printing ink obtained (viscosity: 20 Ford sec.) is used to produce prints on opal glass and aluminium foil. The prints obtained are of good quality. Equally good results may be obtained by using Preparation B6 instead of Preparation D7. 15

4.2. *Aqueous organic printing ink*

20 8.5 parts of Preparation B6
22.5 parts of ethanol and
69 parts of water

25 are homogenized for 15 minutes by means of a toothed disc stirrer without the addition of any other binder. The printing ink so obtained is used to produce prints on paper for laminated sheet materials, and the paper is then laminated and compressed. A two-hour boiling test produces satisfactory results. 25

5. *Spin-coloration of man-made fibres spun from a solution*

5.1. *Viscose*

30 1 part of Preparation D2 is dissolved in
50 parts of water while stirring, and the solution so obtained is stirred into
987 parts of ripened viscose ready for spinning
30 having a cellulose content corresponding to 75 parts. The viscose is then spun into filaments in the usual manner with the aid of a spinning bath containing sulphuric acid. The filaments are subsequently washed in aftertreatment baths (for example, water), desulphurized (for example, with dilute aqueous solutions of Na₂S and NaOH), washed and finished. The filaments obtained display great tinctorial strength, a pure tint, excellent lustre, and a fine and uniform dispersion of the pigment. 35

The preparation may be used in the above process in the form of an aqueous paste as well as in dry form.

40 Equally good results may be obtained by using Preparation A1, C6 or D4, as well as Preparation I1 paste) instead of Preparation D2. 40

5.2. *Polynosic Viscose*

45 Preparation I1 in the form of an aqueous paste based on carbon black (Philblack O) and hydroxyethylcellulose made by method 3d may be successfully employed in a manner analogous to that described under 5.1. for pigmenting high-wet-strength viscose manufactured with the addition of modifiers, which material can be only inadequately coloured by the pigment preparations based on surface-active substances used hitherto. 45

5.3. *Cellophane*

50 The pigmented viscose solutions described under 5.1. used in the manufacture of filaments may also be successfully processed into homogeneously coloured films. Instead of using the preparation in a dry form, it may also be employed in the form of a paste. 50

5.4. *Cellulose triacetate*

55 a) 0.18 part of Preparation B6 is stirred into a spinning solution consisting of
9 parts of cellulose triacetate (Arnel flakes) and
91 parts of a mixture comprising 91 parts of methylene chloride and
9 parts of methanol. 55

A homogeneously pigmented spinning solution in which the pigment is finely and well

dispersed is obtained. Equally good results may be obtained by using Preparation D7 instead of Preparation B6.

b) Homogeneously pigmented spinning solutions may be obtained with Preparations B6 and D7 in the same manner by using, in Example 5.4.a, dimethylsulphoxide instead of the solvent mixture methylene chloride/methanol.

5.5. *PVC fibres*

6 parts of Preparation B6 are stirred into a spinning solution comprising
300 parts of PVC (type TG, Lonza)
700 parts of tetrahydrofuran and
3 parts of Stabilizer Estabex E

and the spinning solution is dry-spun (spinneret temperature: $\sim 57^{\circ}\text{C}$; shaft temperature: $\sim 75^{\circ}\text{C}$; air-stream temperature: 134°C). The spinning process is not impaired in any way. The pigment is finely and well dispersed in the fibres obtained and the fibres display high lustre. Equally good results may be obtained by using Preparation C11, D7 or D13 instead of B6.

5.6. *Polyurethane*

0.2 Parts of preparation B6 is stirred into a spinning solution comprising
10 parts of linear polyurethane (Lycra type) and
90 parts of dimethylformamide.

A homogeneously pigmented spinning solution in which the pigment is finely and very well dispersed is obtained after a short period of time. Equally good results may also be obtained by using Preparation C11 or D7 instead of Preparation B6.

6. *Fibres spin from a melt*

6.1. *Polyamide-6*

98 parts of PA—6 granules (bright Grilon, Emser-Werke) are coated by dry tumbling with

2 parts of Preparation D7 powder,

extruded from the melt at a spinneret temperature of 285°C , and the fibres are stretched at a ratio of 1:3.6. The pigment is finely and very well dispersed in the fibres so obtained.

Equally good results may be obtained by using Preparation D12 or D13 instead of D7.

6.2. *Polyamide—6.6*

98 parts of PA—6.6 granules (Ultramid A3, BASF) are coated with
2 parts of Preparation D12 powder,

extruded from the melt at a spinneret temperature of 300°C , and the fibres are stretched at a ratio of 1:3.6. The pigment is finely and very well dispersed in the fibres so obtained.

Preparations made by the methods described above and which contain the colourants H, P, Q or R are also suitable for melt-coloration of polyamide—6 or polyamide—6.6 in accordance with processes 6.1 or 6.2.

6.3. *Polypropylene*

98 parts of polypropylene granules (Moplen; Montecatini) are coated by dry tumbling with

2 parts of Preparation D7,

extruded from the melt at a spinneret temperature of 288°C , and the fibres are stretched at a ratio of 1:4. The pigment is also finely and very well dispersed in these fibres.

Equally good results may be obtained with Preparation B10 or D13 instead of Preparation D7.

7. *Colouring paper pulp*

7.1 Paper of the following quality is manufactured:

100 parts of bleached sulphite cellulose (40° Schopper-Riegler freeness)

10 parts of kaolin

0.5 part of Preparation D4

2.0 parts of rosin size and

4.0 parts of aluminium sulphate.

The paper is homogeneously coloured and the pigment is finely and well dispersed, even when 1.0 part or 5.0 parts of Preparation D4 are used.

Equally good results may be obtained with Preparations D1 and D7 in the form of aqueous pastes.

7.2. Decorative paper of the following quality is manufactured:

- | | | |
|----|--|----|
| 5 | 100 parts of bleached sulphite cellulose (20° Schopper-Riegler freeness) | 5 |
| | 0.5 part of Preparation C6 | |
| | 20 parts of TiO ₂ | |
| | 2.0 parts of melamine resin 286 (CIBA) | |
| | 4.0 parts of aluminium sulphate | |
| | 2.0 parts of sodium aluminate and | |
| 10 | 0.1 part of Separan NP 10 (Dow Chemicals). | 10 |
- The decorative paper so obtained is compressed in the usual manner to produce good laminates, even when 1.0, 3.0 or 5.0 parts of Preparation C6 are used.
- Equally good results may be obtained by using Preparation D9 instead of C6.

8. *Leather finishes*

- | | | |
|----|--|----|
| 15 | A pigment solution consisting of | 15 |
| | 50 parts of Preparation C7 | |
| | 10 parts of commercial sulphonated castor oil 50% } pasted | |
| | 10 parts of Neocapaderm Finish C, powder (CIBA), | |
| | 250 parts of Capaderm Ground L 9703 (CIBA) and | |
| 20 | 880 parts of water | 20 |
- is applied to buffed chrome side leather in the following manner: —
- | | | |
|----|---|----|
| | 1 coating applied with plush pad, dried, pressed (50°C/150 atm., gauge) | |
| | 4 coatings applied by spraying crosswise, dried, | |
| | 2 coatings of gloss solution 30 g/l of Neocapaderm Finish C Powder applied by spraying; | |
| 25 | Fixation with formaldehyde (1:3) | 25 |
| | Drying and pressing at 80°C/150 atmospheres (gauge). | |

Equally good results may be obtained by using Preparation C3, C11, K1 or K2 instead of Preparation C7. Very evenly pigmented leather is obtained in all cases.

9. *Pigment printing*

- | | | |
|----|---|----|
| 30 | a) A printing paste of the following composition is prepared: — | 30 |
| | 20 parts of Preparation D1 | |
| | 960 parts of Oremasine-Binder-Thickening PLT 15%, consisting of | |
| | 150 parts of Oremasine Binder PLT (CIBA) | |
| 35 | 320 parts of water | 35 |
| | 530 parts of white spirit | |
| | 20 parts of ammonium nitrate/water 1:1. | |
- The paste is applied to mercerized cotton by the screen-printing technique and fixed for 4 minutes at 150°C.
- | | | |
|----|--|----|
| 40 | b) 1 Part of the printing paste described in Example 9a is extended with | 40 |
| | 9 parts of a paste consisting of | |
| | 50 parts of Oremasine Binder PLT (CIBA) | |
| | 10 parts of Oremasine Emulsifier P (CIBA) | |
| | 240 parts of water | |
| 45 | 680 parts of white spirit and | 45 |
| | 20 parts of ammonium nitrate/water 1:1. | |
- The paste is applied to mercerized cotton by the screen-printing technique and fixed for 4 minutes at 150°C.
- Equally good results may be obtained by using Preparation C2 instead of Preparation D1.
- | | | |
|----|--|----|
| 50 | | 50 |
|----|--|----|
10. *Pigment dyeing*
- Cotton 39 is dyed on a padding mangle with the following liquor: —
- | | | |
|----|--|----|
| | 50 parts of Oremasine Binder PLT (CIBA) | |
| | 2 parts of Preparation D1 | |
| | 20 parts of diammonium phosphate/water 1:2 and | |
| 55 | 930 parts of water. | 55 |
- Fixation: 4 minutes at 150°C. A very homogeneous dyeing is obtained.

11. *Dyeings produced with vat dyestuffs*
 Preparations M2, M3, N1, N2 and N3 are applied to cotton by the exhaust process, the pad-steam process (plate steamer) and the pad-jig process, Callebaut - de Blicquy) and Preparation M1 is applied by the exhaust and pad-jig process; very good dyeings are obtained in all cases. 5
12. *Printing with vat dyestuffs*
 12.1 *Normal process*
 Printing paste:
 700 parts of potash thickening (alkaline thickening) 10
 200 parts of water
 80 parts of Hydrosulphite R conc. (CIBA) and
 20 parts of Preparation M2.
 This paste is screen-printed on cotton 39. Fixation: steaming for 8 minutes at 103°C.
 Washing is carried out as follows:— 15
 1st bath: cold rinse
 2nd bath: oxidation
 3rd bath: rinse
 4th bath: soaping at boil
 5th bath: cold rinse.
 Equally good results may be obtained by using Preparation M3, NZ or N3 instead of Preparation M2. 20
- 12.2. *Two-phase process*
 Printing paste:
 650 parts of thickening (Solvitose C5/Polyprint Mullus) 25
 330 parts of water and
 20 parts of Preparation M2.
 This paste is screen-printed on cotton 39. The paste is dried and the material is then padded with
 120 parts of NaOH 36° Bé 30
 65 parts of Rongal A (BASF)
 15 parts of borax and
 800 parts of water.
 Fixation is effected by steaming for 35 seconds at 120°C; washing is carried out in the manner described under 12.1.
 Equally good results may be obtained by using Preparation M3, N1, N2 or N3 instead of Preparation M2. 35
13. *Dyeing with disperse dyestuffs*
 13.1. *High-temperature exhaust process*
 Polyester fibres can be dyed satisfactorily by the high-temperature exhaustion process with Preparations O1 and O2. 40
- 13.2. *Thermosol process*
 Polyester/mercerized cotton fabrics (67:33) can be dyed satisfactorily with Preparation O2, both with and without a thickening agent; it has been observed that the presence of hydroxypropylcellulose brings about an improvement in migration behavior. 45
14. *Printing with disperse dyestuffs*
 The following printing paste:
 20 parts of Preparation O1
 5 parts of Albatex BD (CIBA)
 20 parts of Silvatol I (CIBA) 50
 555 parts of water and
 400 parts of Thickening 301, 12% (CIBA)
 is screen-printed on polyester twill. Fixation is effected in the following manner:
 either by
 a) steaming for 20 minutes at 1.5 atmosphere (gauge), or by
 b) thermofixation for 1 minute at 200°C. 55

Washing is carried out as follows:

1st bath: 2 g/l Hydrosulphite conc. Powder
3 g/l NaOH 36° Bé and
1 g/l Ultravon AN (CIBA)

5 40—50°C, 5—10 minutes,

2nd bath: water only

60°C, 5—10 minutes

3rd bath: cold rinse, water only.

Very good prints are obtained by both methods of fixation.

10 15. *Colouring various kinds of material*

15.1. *Washing powder*

5 parts of a suspension containing 0.25 part of pre-dispersed Preparation B5 are dispersed during a period of five minutes in a suspension consisting of 50 parts of Washing Agent ARSS (mixture of soap and synthetic detergent) and 50 parts of water.

15 The uniformly coloured suspension is dried for 24 hours at 90°C under a pressure of 400 mm Hg and the dried material is granulated. The product is uniformly coloured. Equally good results may be obtained by using Preparation B8 or B7 or Preparation D6 in the form of the aqueous grinding batch prior to working up, as obtained in Process 3a.

20

15.2. *Soap*

100 parts of soap base (mixture consisting mainly of Na-palmitate and Na-stearate)

0.05 parts of ethylenediaminetetracetic acid

25 0.1 part of TiO₂ and

5.0 parts of a suspension containing 0.1 part of pre-dispersed Preparation B1 are kneaded in a kneading apparatus and processed into bars of soap in the usual manner. The soap is satisfactorily coloured. Equally good results may be obtained by using Preparation B5, D1 or D7 or Preparation D6 in the form of the aqueous grinding batch prior to working up, as obtained in Process 3a.

30 The following words used in the above examples are registered Trade Marks:

SOLVITOSE, HOSTALEN, ULTRAVON, CELLIDOR, CIBAMIN, CELLOPHANE, KRONOS, MOPLIN, RONGAL, DESMOPHEN, DURAPLEX, GRILON, MODOCOLL, PROPATHENE, PLEXIGUM, DESMODUR, ARNEL, LYCRA, ALBATEX, CYCLOLAC, VESTAMID, DESMORABIT, ESTABEX, SEPARAN and CAPADERM.

35

WHAT WE CLAIM IS:—

1. Solid dry dyestuff preparations which contain at least one finely divided water-insoluble colorant and at least one hydroxyalkylcellulose ether (as herein defined) and in which the weight ratio of colorant to cellulose ether is at most 9:1.

40 2. Preparations as claimed in claim 1, wherein the hydroxyalkylcellulose ether is free from ionic groups and is soluble in water and/or in liquid alcohols, ketones and esters.

3. Preparations as claimed in claim 1 or claim 2, wherein the hydroxyalkylcellulose ether is a hydroxyethylcellulose ether.

45 4. Preparations as claimed in claim 1 or claim 2, wherein the hydroxyalkylcellulose ether is a hydroxypropylcellulose ether.

5. Preparations as claimed in claim 1 or claim 2, wherein the hydroxyalkylcellulose ether is a hydroxyethylhydroxypropylcellulose ether.

6. Preparations as claimed in any one of claims 1 to 5, wherein the hydroxyalkylcellulose ether is an alkylhydroxyalkylcellulose ether.

7. Preparations as claimed in any one of claims 1 to 6, which also contain a surface-active compound and/or a plasticizer.

8. Preparations as claimed in any one of claims 1 to 7, in which the weight ratio of colorant to cellulose ether is from 9:1 to 1:4 or from 4:1 to 1:4.

55 9. Preparations as claimed in any one of claims 1 to 8, in which the water-insoluble colorant is a pigment.

10. Pigment preparations as claimed in claim 9, in which the major proportion by weight of the pigment has a particle size of 1 μ and below.

60 11. Preparations as claimed in any one of claims 1 to 8, in which the water-insoluble colorant is a vat dyestuff.

60

12. Preparations as claimed in any one of claims 1 to 8, in which the water-insoluble colorant is a disperse dyestuff.

13. Any one of the preparations as claimed in claim 1 and which is described in the examples herein.

5 14. A process for the manufacture of solid, dry dyestuff preparations as claimed in claim 1, wherein a water-insoluble colorant is mixed with a hydroxyalkylcellulose ether in the absence or presence of liquids and, if necessary, the mixture is ground or kneaded and dried. 5

10 15. A process as claimed in claim 14, wherein the hydroxyalkylcellulose ether is free from ionic groups and is soluble in water and/or liquid alcohols, ketones and esters. 10

16. A process as claimed in claim 14, wherein the colorant and hydroxyalkylcellulose ether are mixed in an aqueous medium.

15 17. A process as claimed in claim 14, wherein the colorant and hydroxyalkylcellulose ether are subjected to grinding in an aqueous medium. 15

18. A process as claimed in claim 14 or claim 15, wherein the colorant and hydroxyalkylcellulose ether are kneaded in a kneading apparatus in the presence of liquids which dissolve the hydroxyalkylcellulose ether and, if necessary, in the presence of comminuting agents.

20 19. A process as claimed in claim 14, wherein the water-insoluble colorant is ground in a liquid medium and subsequently a hydroxyalkylcellulose which is soluble in the said medium is added. 20

20. A process as claimed in any one of claims 14 to 19, wherein at least one surface-active compound and/or plasticizer is added prior to, simultaneously with or subsequent to the hydroxyalkylcellulose. 25

25 21. A process as claimed in any one of claims 14 to 20, wherein a mixture obtained in liquid form is dried by evaporation, spray-drying or freeze-drying.

22. A process as claimed in claim 14, wherein the preparation is prepared by precipitating the cellulose ether out of a solution on to the colorant or colorants suspended in the said solution in a state of fine division and the precipitated preparation is isolated by filtration and freed from adherent liquid. 30

23. A method of pigmenting thermoplastic synthetic materials, wherein there is used a preparation as claimed in any one of claims 1 to 10.

24. A method as claimed in claim 23, wherein the thermoplastic synthetic material is made of polyvinyl chloride, polyethylene, polypropylene, polystyrene, a polymethacrylate, a polyurethane, a polyamide or a cellulose acetate. 35

25. A method of pigmenting paints and lacquers that may be diluted with water, wherein there is used a preparation as claimed in any one of claims 1 to 10.

26. A method of pigmenting paints and lacquers based on organic solvents, wherein there is used a preparation as claimed in any one of claims 1 to 10. 40

27. A method of pigmenting printing inks that may be diluted with water, wherein there is used a preparation as claimed in any one of claims 1 to 10 and 12. 40

28. A method of pigmenting printing inks based on organic solvents, wherein there is used a preparation as claimed in any one of claims 1 to 10 and 12.

29. A method of pigmenting man-made fibres by spin-pigmentation, wherein there is used a preparation as claimed in any one of claims 1 to 10. 45

30. A method for the melt-coloration of polyamide or polyolefine fibres, wherein there is used a preparation as claimed in any one of claims 1, 2 and 4 to 10.

31. A method of colouring by spin-coloration regenerated cellulose fibres spun from an aqueous solution, wherein there is used a preparation as claimed in any one of claims 1 to 10. 50

32. A method of colouring by spin-coloration polyvinyl chloride, polyurethane or cellulose triacetate fibres spun from a suitable solvent, wherein there is used a preparation as claimed in any one of claims 1, 2 and 4 to 10.

33. A method for the mass-coloration of films produced from melts or aqueous or organic solutions, wherein there is used a preparation as claimed in any one of claims 1 to 10. 55

34. A method of colouring paper, wherein there is used a preparation as claimed in any one of claims 1 to 10.

35. A method of pigmenting leather finishes, wherein there is used a preparation as claimed in any one of claims 1 to 10. 60

36. A method of pigmenting printing pastes or dye-liquors to be used in the pigment printing or pigment dyeing of woven, knitted or non-woven textiles, wherein there is used a preparation as claimed in any one of claims 1 to 10.

37. A method of pigmenting cement, wall and ceiling plaster, soaps, waxes, coloured pencils, inks and water-colour paints, or cosmetic preparations, wherein there is used a preparation as claimed in any one of claims 1 to 10.

5 38. A method of dyeing or printing woven, knitted or non-woven textile fabrics by a dyeing or printing process suitable for the application of vat dyestuffs or disperse dyestuffs to such materials, wherein there is used a preparation as claimed in any one of claims 1 to 8, and 11 or 12. 5

39. Materials which have been pigment dyed or printed by a process as claimed in any one of claims 23 to 38.

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